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SOME PROBLEMS RELATED TO CLEANUP OF PARATHION-CONTAMINATED SURFACES FOLLOWING SPILLAGE

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INTRODUCTION

The potential problem of contamination of foodstuffs, feeds, clothing, and other consumer goods by toxic pesticides during transportation or storage continues to be of concern even though there has been considerable effort directed toward the prevention of such incidents. One concern is the proper decontamination of surfaces such as floors of warehouses, loading docks, trucks, and railroad cars so that there is no hazard from direct contact by human beings and animals or indirectly through contamination of items placed on surfaces.

The organophosphorus pesticide, parathion, when shipped in liquid formulations, has been one of the greatest offenders in the past as far as spillage of highly toxic liquid pesticides during transportation and storage is concerned. Experience with several pesticide spills, including attempted decontamination, has renewed the need to review the subject matter and conduct additional decontamination studies. Decontamination information in various publications suggest or recommend several absorbents, decontamination chemicals, and procedures;[1,2] however, details on comparative efficiency of the decontamination materials, especially in relation to specific procedures or techniques in their use are, in most cases, inadequate or lacking.

The purpose of the present paper is to discuss decontamination problems encountered in actual spillage incidents and to report results of the first phase of a series of research studies being carried out on evaluation of decontamination materials and techniques. This phase involves certain absorbents and chemicals that are readily available in most areas and includes some of those that have most commonly been suggested for cleanup and decontamination of toxic pesticide spills.

Materials and Methods

Decontamination materials used in experiments on flooring of truck trailers were solutions of household bleach (5.25% sodium hypochlorite) and lye (96% sodium hydroxide). Sampling to determine the level of parathion in the air of a contaminated vehicle was carried out with midget impingers, containing 95% ethanol as a solvent. Checking of flooring for surface contamination followed the flour sack technique or alcohol swabbing procedures described below for controlled studies of test surfaces.

In studies involving experimental test surfaces, absorbent materials used for initial pickup of excess liquid pesticide to prevent enlargement of a contaminated area were attaclay, anhydrous filler, light sandy loam soil, and fine sawdust. The attaclay and anhydrous filler were chosen because such fine clays are considered highly adsorbent. The soil was chosen because it is usually the most readily available material. Sawdust was chosen primarily because it has been used in several pesticide spillage incidents.

Degradation chemicals used were liquid household bleach (sodium hypochlorite), household drain cleaner (sodium hydroxide as a saturated solution), washing soda (sodium carbonate slurry), hydrated lime (calcium oxide slurry), liquid household detergent, and ethyl alcohol. These chemicals were used in various combinations; all have been used in actual spillage incidents.

Test surfaces were 30 cm square pieces of oak, fir, fir plywood, diamond plate steel, smooth aluminum, and concrete. Putty caulking strip material was applied to the borders of the test surfaces to confine 7 ml of 46% emulsifiable concentrate parathion on the test surface area.

The procedure for comparing the efficiency of absorbent materials was as follows: emulsifiable concentrate parathion was applied to the test surface and allowed to soak into it for three 5, 10, and or 60 minutes. Absorbent material was then added to the surfaces and allowed to stand for one hour. The absorbent was removed and analyzed for parathion content; the percent of applied parathion recovered was calculated.

The procedure for comparing the efficiency of chemicals used for physical cleanup and chemical degradation was as follows: 46% emulsifiable concentrate parathion was applied and allowed to soak into test surfaces for one hour. A generous amount of attaclay was then deposited on the surfaces and left for one hour to absorb the pesticide. The absorbent was re-

moved and a generous amount of decontamination chemical was added to the test surfaces. The surface was scrubbed for approximately 15 seconds and allowed to stand for 15 minutes. The next step was a thorough water flushing. The chemical treatment and water flushing were repeated a second time.

After decontamination and water flushing, the test surface was allowed to dry for four hours. It was then either thoroughly swabbed with 95% ethanol-impregnated gauze swabs to measure the amount of pesticide recoverable by that technique or checked for contamination potential by use of small test flour sacks placed on the surface for a 48-hour period. The test sacks were of unbleached muslin and contained 60 grams of flour each with 35 sq cm surface contact area.

The amount of pesticide found in both the flour and sack material were added. The flour sack technique was used to closely simulate contamination of an item having maximum absorbency.

The analysis for parathion was by electron-capture gas liquid chromatography. The presence of parathion in certain samples was confirmed by use of a flame photometric detector.

Spillage Incidents

Experimentation with wood flooring from several vehicles that had been contaminated with liquid pesticides during transportation spillage incidents has provided information which points out certain problems related to adequate cleanup and decontamination. Two examples are as follows:

Incident No. 1

Leakage of 44.5% emulsifiable concentrate parathion from a metal drum resulted in contamination of oak flooring in a truck trailer. The initial contaminated area was estimated to be about 45 cm in diameter. By the time research personnel learned of the spillage and obtained permission to conduct tests, trucking company personnel had already carried out a cleanup procedure which they felt was adequate.

First, they removed as much of the excess pesticide as possible with sawdust and cedar shavings. After this absorbent material had been left on the contaminated area for about 40 minutes, it was removed and approximately 2.27 kg (5 lbs) of baking soda (sodium bicarbonate) were placed on the surface. Water was added and the area vigorously scrubbed with a stiff broom. The floor was then thoroughly flushed with water.

After the flooring dried an oily appearing area about one meter square was evident, indicating a spreading of the more concentrated material during the attempted cleanup operations. Analysis of surface swab samples indicated that from 0.30 to 0.84 mg of parathion per sq cm was available at the surface even after cleaning. It was evident that the cleanup operation was inadequate.

Trucking company personnel had not noticed whether or not the pesticide had penetrated the flooring and subflooring material to the undercarriage below. It was obvious however, that replacement of contaminated flooring and subflooring would be necessary.

Even though the decision to replace contaminated flooring materials was reached, research personnel took advantage of the situation to conduct surface decontamination tests. The area of apparent maximum floor contamination was divided in half. One portion was thoroughly soaked with household bleach and then scrubbed with a stiff broom. The other was thoroughly scrubbed, using lye and water. The entire

TABLE 1: Efficiency of Readily Available Chemicals for Cleanup of Parathion-Contaminated Surfaces as Determined by Flour Sack and Swabbing Techniques[a]

Surface	Parathion Recovery from Surfaces Following Decontamination Treatments[b] (mg/sq cm of each surface as indicated)[c]									
	Household Bleach		Household Dish Cleaner		Household Dish Cleaner Plus Bleach		Washing Soda		Lime	
	Flour Sack	Alcohol Swab	Flour Sack	Alcohol Swab	Flour Sack	Alcohol Swab	Flour Sack	Alcohol Swab	Flour Sack	Alcohol Swab
Aluminum alloy (smooth)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Diamond plate (steel)	1.6	0.9	1.7	1.1	1.5	0.7	1.8	0.8	1.9	1.1
Oak flooring	19.1	160.7	13.1	161.2	12.1	15.1	42.8	225.2	102.9	229.9
Fir flooring	20.6	120.4	61.6	125.1	10.2	11.4	40.1	151.8	115.2	267.2
Fir plywood	20.1	124.1	17.8	119.0	13.1	9.9	29.1	158.1	117.2	199.9

[a] 45% EC parathion allowed to soak into surface for one hour followed by pickup with absorbent prior to chemical decontamination treatment.
[b] Two rough scrubbings with decontamination solutions plus water rinses.
[c] Each value is average of 3 replicates. Flour sack values include both flour and sack material contamination resulting from 48-hour surface contact.

floor area was then thoroughly flushed with water and allowed to dry overnight.

Swab samples were taken at different locations to determine if parathion was available at the surface in either of the test decontamination areas. In the area where the decontamination process had used household bleach, from 0.20 to 0.28 mg/cm² was recovered from the surface; where lye was used the recovery was less than 0.16 to 0.40 mg/cm². It was evident that satisfactory decontamination at the surface had not been accomplished using lye. As a result of this spillage incident, the flooring was replaced and contaminated undercarriage parts were steam cleaned, with all soil contaminated by drainoff water collected and buried.

Incident No. 2

Spillage of liquid parathion in a truck trailer during transportation provided another opportunity to conduct decontamination experiments. The spout seal of a 3.79 liter (one-gallon) drum of flowable parathion broke loose when a case of four drums fell to the floor as the load shifted. Practically the entire contents of the drum leaked onto the oak flooring, contaminating an area approximately 1 m by 1.3 m. Three cardboard cartons containing glassware, shoes, and miscellaneous drug items showed indications of surface contamination where they contacted the flooring in the spill area. Contact time during transportation was estimated to be approximately three hours; the cartons and contents were destroyed.

A pesticide decontamination team had attempted to clean the floor by scrubbing with household liquid bleach, followed by water flushing. The manager of the trucking company agreed to leave the vehicle in place for several days so that cleanup tests could be conducted. Swab samples of the floor surface taken at different locations on the areas of greatest contamination showed values up to 1.9 mg of parathion per square cm. Repeated swabbings of the same areas at 3, 9, 13, and 14 days following spillage and cleanup indicated that approximately as much parathion could be recovered from the surface at the 14-day period as was recovered initially. These data indicated that a relatively large quantity of parathion had soaked into the flooring. It was apparent that the soaking and scrubbing with household bleach did not result in adequate cleanup.

An experiment was also conducted to determine the potential for absorption of the toxic material by items placed on the contaminated floor area. Sacks of flour were placed on contaminated surfaces at locations adjacent to the swab test areas. It was felt that the sacks of flour would provide greater absorption of toxic material from the flooring than other items that might contact the surface. Thus, any recommendations derived from these tests would be conservative. After 8 hours of surface contact the amount of parathion recovered from the test sacks ranged from 1.0 to 2.8 mg/cm². Recovery following a 72-hour contact period ranged from 2.8 to 13 mg/cm². These results indicate that if the vehicle had been used, there would have been a potential hazard of contamination of items placed on the flooring. Fortunately, the trucking company followed the suggestion that the flooring be replaced before the truck be used again.

TABLE II: Parathion Contamination of Test Floor Sacks Set on Surface Following Cleanup Procedure Using Various Decontamination Materials[a]

Surface	Parathion Recovery (µg/cm²)[b]			
	Bare Wood (Oak)	Smooth Aluminum	Packing Soil	Lime
Concrete[c]	10.1	6.1	1.8	1.8
Oak flooring	3.1	19.9	21.1	12.2
Fir flooring	7.9	26.3	20.1	17.1
Fir plywood	8.9	23.8	12.5	11.8
Sheet plastic	6.8	0.8	0.7	0.7

[a] 10 parathion allowed to soak into surface one hour before test piece with absorbent was set to contact decontamination treatment. [b] Due to limits of precision, values with two significant digits are considered to have a single significant figure. [c] Surface to surface type of concrete loading dock surface.

Another concern was the amount of volatile toxic material that might be in the air within a closed truck during shipment, especially under conditions of high summer temperatures. Also, when a truck is opened at destination, workers might inhale toxic vapors before the truck is properly ventilated.

Air samples were taken in the truck-trailer. Parathion content of air 30.5 cm (1 ft) above the surface of greatest contamination was 0.019 mg/M³. At 168 cm (5½ ft) the level was 0.001 mg/M³. During sampling the floor surface temperature was 29°C (85°F) and the ambient air in the trailer with rear doors open was 28°C (83°F).

After the trailer doors had been closed for one hour, the floor surface temperature was 41°C (105°F) and ambient air temperature was 39°C (103°F). At that time, the concentration in the air was 0.035 mg/M³ at 30.5 cm and 0.031 mg/M³ at 168 cm. These levels of parathion are below the 0.1 mg/M³ value set by the Committee on Threshold Limits, American Conference of Governmental Industrial Hygienists[1] as the maximum level to which workers should be exposed for an 8-hour working day.

Test Surface Results

Results of controlled tests to compare efficiency of absorbent materials indicated that attaclay was the most effective. Anhydrous filler was next in efficiency, followed by light sandy loam soil and fine sawdust.

The greatest recovery was from smooth aluminum alloy from which all absorbent materials recovered more than 90% of the parathion. This high degree of recovery could be attributed to the inability of the

liquid pesticide to penetrate the relatively smooth metal surface.

Recovery of pesticide by the absorptive materials was less on concrete surfaces than on wood surfaces. Recovery from concrete, using the most efficient material, attaclay, was 1.7, 0.9, and 0.1% of the applied parathion at 5, 30, and 60 minutes, respectively, following simulated spillage. Recovery from oak surfaces with attaclay ranged from 39.8 to 42.4% with no great difference in values for the 5, 30 and 60 minute periods. When soil was used as the absorbent, the recovery from oak ranged from 13.7 to 17.8% of the applied dosage. Values for the sawdust tests ranged from 19.2 to 31.5%. Recovery from fir surfaces was less with soil and sawdust than with attaclay or anhydrous filler.

The efficiency of readily available chemicals for cleanup and decontamination of parathion-contaminated metal and wood surfaces, as determined by the swabbing and flour sack techniques for pesticide recovery, are shown in Table I. Lower tabulated values show that less pesticide was available at the test surface, indicating more efficient cleanup. The exceptionally low values for aluminum alloy and diamond plate steel indicate relatively good cleanup of those surfaces. Because the absorbent is able to remove a high percentage of the pesticide cleanup may be accomplished by physical means. The slightly higher values obtained for diamond plate steel as compared to those for aluminum were probably due to small amounts of toxicant being trapped at the surface in very small pock marks that appeared to have been caused by normal weathering or oxidation; this condition is observed on most transportation vehicles using this material for flooring or as part of the tailgate assembly.

In the case of wood surfaces much more parathion was recovered by sampling, indicating less efficient cleanup. More was recovered by the alcohol swabs than by the flour sack technique except where household drain cleaner and household bleach were used in combination. The greater recovery by the swab technique may be due to the action of the alcohol in moving more deeply penetrated pesticide to the surface during the swabbing operation. The reason for practically no difference in recovery values for both test techniques where the combination of household cleaner and household bleach was used is not clear. Perhaps relatively strong chemical degradation action of both materials may have reached to a greater depth in the wood surfaces than occurred when each chemical was used alone. Also, the parathion oxidation product, paraoxon, is hydrolyzed by strong alkali more rapidly than is parathion, and the bleach would favor conversion to paraoxon.

Although test sacks of flour may have some effect of drawing pesticide to the surface, it would no doubt be much less than occurs as a result of swabbing with ethanol, and probably the amount of pesticide taken up by the flour and sack more closely represents the potential for maximum contamination of articles placed on contaminated surfaces. Based on the degree of contamination of test sacks of flour set on the surfaces following cleanup and decontamination procedures, the combination of household drain cleaner and household bleach produced better results than either of those chemicals used alone. However, when used either singly or in combination, they gave better results than washing soda and much better results than where lime was used.

Unfortunately, there were no tests beyond the 48-hour flour sack contact time to indicate whether or not appreciable quantities of pesticide would continue to rise to the surface of the wood as was indicated above in tests of a truck-trailer floor in spillage Incident No. 3.

Results of a second series of tests conducted on concrete, oak, fir, and diamond plate steel surfaces using the same decontamination chemicals, but eliminating the combination household drain cleaner-household bleach treatment, are shown in Table 2. Only the flour sack technique was used as the criterion for estimating cleanup efficiency. The data indicate that all of the decontamination chemicals gave best results on diamond plate steel. Less desirable results were obtained on the wood and concrete surfaces. On the wood test surfaces, household bleach produced better results than other chemicals; however, the amount of pesticide recovered by the flour sack technique was probably too great to be considered acceptable as a safe level. Bleach was less effective on concrete than were the others.

TABLE III: Parathion Contamination of Test Flour Sacks Set on Oak Surface Following Cleanup Procedure Using Various Decontamination Materials[a]

Decontamination material	Parathion Recovered (ppm)[b]	
	30 min	48 hr
Liquid household bleach	5.9–8.8	5.8
Liquid household plus soap	1.2–1.9	6.7
Liquid household plus powdered drain cleaner	7.7–11.6	11.8
Liquid household plus powdered drain cleaner	15.0–26.2	19.6
Household drain cleaner	19.8–32.8	28.7
Soap and alcohol	25.9–38.4	26.5
Soap and alcohol plus powdered drain cleaner	0.3–0.4	11.2
Liquid household plus powdered drain cleaner	14.6–81.3	61.6

[a] Test sacks of parathion allowed to soak into surface for 30 min, followed by pickup with attaclay or soil, application of chemical decontamination treatment, and pickup with 3 successive applications. Includes spillage and soil material contamination results (average of 3 replicates). Surface contact.

A third series of tests (Table III) was conducted to determine the effect of additional materials. Various materials or combinations of materials were tried on oak with pesticide absorption by test flour sacks again being used to determine the availability of toxic ma-

terial at the test surface. The data indicate that both the liquid household bleach treatment and the liquid detergent plus water treatment produced better results than other materials or combinations of materials.

Contamination of the test flour sacks set on the surfaces following cleanup was approximately the same for these two processes with average recovery values ranging from 5.9 to 8.8 ppm for bleach and 5.7 to 7.9 ppm for the detergent plus water treatment. Values obtained when bleach and detergent were used in combination indicated slightly less cleanup efficiency. Much poorer results were obtained when drain cleaner, alcohol, or mixtures of alcohol and detergent, bleach, or drain cleaner were used, and poorest results were obtained where detergent and drain cleaner were used in combination (46.4 to 83.3 ppm recovery). The poor results with certain combinations may indicate that the chemicals do not mix well or in some other way are not very effective in removing parathion from oak surfaces. The liquid household bleach, as well as the household drain cleaner treatments, resulted in approximately the same average values as noted in Table II for oak in the second series of tests.

CONCLUSIONS

Certain absorbent clays such as attaclay may be efficient for containment and absorption of liquid pesticide spills; however, unless such special materials are readily available near a spillage site, it would be advisable to use soil or any other immediately available absorbent material because emulsifiable concentrate formulations of pesticides are able to rapidly penetrate wood or concrete. Thus, quick containment and absorption of spills is an important factor in cleanup operations.

Experience with truck-trailer incidents, as well as research using test surfaces, indicates that when a spill of liquid pesticide occurs on wood flooring, the contaminated flooring should be removed and replaced because adequate decontamination of wood appears to be difficult, if not impossible, to accomplish. Even where a small spill occurs within the bounds of a single board width, tests have shown that pesticide penetrates the board surface and may move within resin ducts and rise to the surface some distance from the spill site, producing another surface-contaminated area.

Although it appears to be possible to adequately decontaminate smooth metal surfaces, additional difficulties arise when spillage on metal truck floors soak through seams or around bolts to the subflooring material below.

Decontamination tests on concrete surfaces gave less than satisfactory results. Since, in many cases, it is almost impossible to remove and replace contaminated concrete, additional research is needed to develop more efficient procedures for making contaminated concrete surfaces safe.

There may not be a need for the use of stronger decontamination chemicals such as sodium hydroxide or sodium hypochlorite, especially in the initial stages of spillage cleanup because physical removal may outweigh effective chemical action in the short time usually involved. Chemical degradation may be more useful as a follow-up for detoxifying pesticide on surfaces where the physical cleanup procedure has not resulted in safe levels.

The handling of lye is a hazard because of its highly caustic nature. When household bleach has been applied to concentrated parathion, there is a possibility that additional amounts of the parathion oxidation product, paraoxon, may be produced. Preliminary experiments indicate that when parathion and bleach are mixed on a concrete surface, as much as 30% of the parathion is the more acutely toxic paraoxon. Thus, avoiding excess usage of such materials is probably a wise approach to cleanup of toxic parathion spillages.

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